

Phase Transitions of Organic-Inorganic Hybrid Perovskites under PressureY. Lee, T. Vogt (BNL-Physics), J. A. Hriljac (Univ. Birmingham, UK), D. B. Mitzi (IBM)
Beamline(s): X7A

Hybrid perovskites, based on a molecular-scale composite of inorganic and organic components, provide a substantial opportunity for tailoring combined functionality within a single material or new phenomenon that result from the interaction between the organic and inorganic subunits. These form a diverse structural group in which the effective dimensionality of the inorganic framework can be controlled from zero-dimension to layered oriented systems.¹ The ordering and hydrogen bonding of the organic cations are known to change as a function of temperature and give rise to various structural phase transitions. Knowledge on pressure-induced changes in the organic-inorganic interaction and its structure is, however, scarce, and we have initiated a systematic study to explore the high-pressure behaviors of various hybrid perovskites using monochromatic synchrotron X-ray and a diamond-anvil cell. Three samples in 3D hybrid perovskite systems, $(\text{CH}_3\text{NH}_3)\text{SnI}_3$, $(\text{NH}_2\text{CH}=\text{NH}_2)\text{SnI}_3$, $(\text{CH}_3\text{NH}_3)_{0.5}(\text{NH}_2\text{CH}=\text{NH}_2)_{0.5}\text{SnI}_3$, were chosen to investigate the effect of varying number of hydrogen-bonding site per A cation on its pressure response. As pressure increases above 0.5 GPa, all these materials show doubling of their cubic cell edges, mainly due to the tilting of the respective SnI_3 framework. The supercell structure of $(\text{CH}_3\text{NH}_3)\text{SnI}_3$ transforms to an orthorhombic phase above 3.0 GPa, probably as a result of increased ordering of the organic cation, whereas those of $(\text{NH}_2\text{CH}=\text{NH}_2)\text{SnI}_3$ and $(\text{CH}_3\text{NH}_3)_{0.5}(\text{NH}_2\text{CH}=\text{NH}_2)_{0.5}\text{SnI}_3$ transform into tetragonal phases above 1.5 GPa and 1.0 GPa, respectively. In all cases, further increase in pressure above 4 GPa results in amorphization, which is reverted upon pressure release. This suggests the organic cations act as a template under high pressure and impart structural memory effect during amorphization of the inorganic frameworks.

Figure. Pressure dependence of the unit cell edge lengths of $(\text{CH}_3\text{NH}_3)\text{SnI}_3$ (upper), $(\text{NH}_2\text{CH}=\text{NH}_2)\text{SnI}_3$ (middle) and $(\text{CH}_3\text{NH}_3)_{0.5}(\text{NH}_2\text{CH}=\text{NH}_2)_{0.5}\text{SnI}_3$ (lower).

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